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TITLE: Nickel@ concentration measurement method by absorptiometry, for electroless nickel plating liquid - involves irradiating plating liquid by red light source which emits light beam having specified longer and shorter wavelength

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PATENT-FAMILY:

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ABSTRACTED-PUB-NO: JP 10142143A

BASIC-ABSTRACT:

The method involves irradiating an electroless nickel plating liquid using a red colour light source. The light source emits light beam whose shorter wavelength ranges from 600-650 nm and longer wavelength lies within 750-800 nm. The nickel concentration is obtained based on the output of an optical receiver that receives light beam passing through the electroless plating liquid.

ADVANTAGE - Offers easy changing of light source. Enables accurate measurement.

CHOSEN-DRAWING: Dwg.1/4

TITLE-TERMS: NICKEL@ CONCENTRATE MEASURE METHOD ELECTROLESS
NICKEL PLATE LIQUID

IRRADIATE PLATE LIQUID RED LIGHT SOURCE EMIT LIGHT BEAM
SPECIFIED

LONG SHORT WAVELENGTH

DERWENT-CLASS: E31 J04 M13 S03

CPI-CODES: E11-Q03L; E35-W; J04-C03; M13-B;

EPI-CODES: S03-E04A1;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

Fragmentation Code

A428 A940 A960 A970 C710 C730 M411 M417 M424 M740

M750 M903 M904 N102 N141 Q435 Q454 Q463

Specific Compounds

11235A

Chemical Indexing M3 *02*

Fragmentation Code

A428 A940 A960 A970 C710 C730 M411 M417 M424 M740

M750 M903 M904 N102 N141 Q435 Q454 Q463

Specific Compounds

19540A

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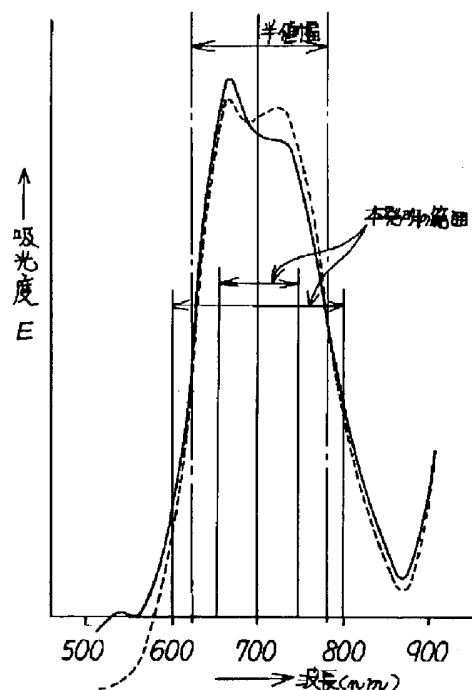
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(54) 【発明の名称】 無電解ニッケルめっき液のニッケル濃度測定方法

(57) 【要約】

【課題】 ターン数が進んでも吸光度法により正確にニッケル濃度を測定することができる無電解ニッケルめっき液のニッケル濃度測定方法を提供する。

【解決手段】 無電解ニッケルめっき液のニッケル濃度を吸光度法により測定するための赤色光源として、中心波長値が690～700nm、半値幅の短波長値が600～650nm、長波長値が750～800nmである連続スペクトル光源を用いる。これによりターン数の進行に伴う吸収曲線の形状変化の影響を無くし、誤差の少ないニッケル濃度の測定が可能となる。



【特許請求の範囲】

【請求項1】 無電解ニッケルめっき液のニッケル濃度を赤色光源を用いて吸光光度法により測定するにあたり、この赤色光源として半値幅の短波長値が600～650nm、長波長値が750～800nmである連続スペクトル光源を用いることを特徴とする無電解ニッケルめっき液のニッケル濃度測定方法。

【請求項2】 中心波長値が690～700nmである赤色光源を用いる請求項1に記載の無電解ニッケルめっき液のニッケル濃度測定方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、吸光光度法による無電解ニッケルめっき液のニッケル濃度測定方法に関するものである。

【0002】

【従来の技術】無電解ニッケルめっきでは、めっき液中のニッケルイオンがワーク金属の触媒還元反応によりワーク表面にニッケル金属として析出し、それにつれてニッケル濃度、還元剤濃度、pH等が徐々に低下して行く。*20

*そのため、めっき液をサンプリングして吸光光度法によりニッケル濃度を測定し、めっき液中のニッケル量等を常に定められた値に保つめっき液管理が行われている。

【0003】この吸光光度法によるニッケル濃度測定は、ニッケルイオンの吸収波長付近の波長を持つ赤色光源を用いて行われており、多くの場合フィルターにより波長領域を710±10nmの狭い範囲に絞られた赤色光源が用いられている。ところがこの方法で測定されたニッケル濃度は建浴時には実際のニッケル濃度（化学分析値）と一致しているが、ターン数（使用度）が進むと誤差が大きくなるという問題があった。その原因は、めっき液が老化して行くと亜リン酸、硫酸ソーダ等の不純物が蓄積することにより色調の変化が生じ、またターン数の進行に伴うpHの変化によっても色調の変化が生じるためである。参考のため、表1と表2に波長領域710±10nmの場合におけるターン数とpHの変化による吸光度の変化の一例を示す。

【0004】

【表1】

ターン数	めっき液分析値(g/L)			吸光度
	ニッケル	NaH ₂ PO ₄ ・H ₂ O	NaHPO ₃ ・5H ₂ O	
0	6.7	29.2		0.356
2.25	6.7	32.1	157.3	0.368
5.07	6.7	25.8	372.5	0.383
7.51	6.7	17.3	571.1	0.402
9.03	6.7	14.2	656.5	0.407

【表2】

ニッケル濃度(g/L)	pH	吸光度
3.79	4.20	0.20551
3.79	4.60	0.20901
3.79	5.01	0.21042

【0005】

【発明が解決しようとする課題】本発明は上記した従来の問題点を解決し、ターン数が進んでも吸光光度法により正確にニッケル濃度を測定することができる無電解ニッケルめっき液のニッケル濃度測定方法を提供するためになされたものである。

【0006】

【課題を解決するための手段】上記の課題を解決するためになされた本発明は、無電解ニッケルめっき液のニッケル濃度を赤色光源を用いて吸光光度法により測定するにあたり、この赤色光源として半値幅の短波長値が600 ※50

※～650nm、長波長値が750～800nmである連続スペクトル光源を用いることを特徴とするものである。なお、その中心波長値は690～700nmであることが好ましい。このように、従来の吸光光度法が中心波長±10nmの狭い範囲に絞られた赤色光源を用いていたのに対して、本発明は半値幅を100～200nmという広い幅とした連続スペクトル光源を用いた点にポイントがある。

【0007】

40 【発明の実施の形態】以下に本発明の好ましい実施の形態を示す。図1は吸光光度法の測定原理図であり、1は赤色光源、2はサンプリングされた無電解ニッケルめっき液、3は受光器である。赤色光源1から無電解ニッケルめっき液2に照射される入射光量を I_0 とし、受光器3に入る透過光量を I_t とすると、 $t = I_t / I_0$ を透過率といい、 $E = \log(1/t)$ を吸光度という。そして図2に示すように一般にニッケル濃度は吸光度 E に正比例するので、吸光度 E から無電解ニッケルめっき液中のニッケル濃度を求めることができる。

【0008】しかし、前記したとおりターン数が進むと

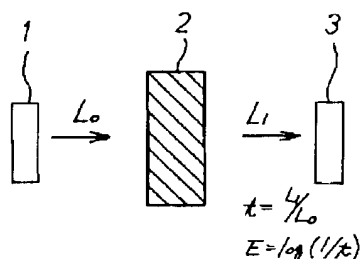
不純物イオンが蓄積したりpHが変化するため、図3に示すように化学分析により求められたニッケル濃度が一定であるにもかかわらず、吸光度から求めた濃度が増加して測定誤差を生じる。本発明者等はこの吸光度の変化について検討した結果、無電解ニッケルめっき液の吸光曲線の形状が、ニッケル濃度が一定であるにもかかわらずターン数が進むと図4のように変化することを解明した。

【0009】即ち、吸光曲線は建浴時（ターン数0）のときは図4の実線の形状であるが、ターン数5.07のときは図4の鎖線の形状に変化する。そのために従来の710±10nmの波長領域の赤色光源を用いた方法では、ニッケル濃度が一定であるにもかかわらず、ターン数が進むと吸光度Eが変化する結果となる。

【0010】これに対して本発明では赤色光源1として、半値幅の短波長値が600～650nm、長波長値が750～800nmである連続スペクトル光源を用いる。この波長領域は、図4に破線で示す吸光曲線の半値幅にほぼ相当するものである。図4に示されるように、吸光曲線の形状はターン数が進むと増加する部分と減少する部分とがある。受光器3に入る透過光量 I_t は赤色光源1の最短波長値から最長波長値までの区間の積分値であるから、本発明のような広い波長領域にわたる連続スペクトル光源を用いて吸光度の測定を行えば、ターン数が進むと増加する部分と減少する部分とが打ち消し合い、ほぼ一定の吸光度を得ることができる。

【0011】赤色光源1の半値幅の短波長値が600nm未満となったり長波長値が800nmを越え、ニッケル濃度に対する感度が低下する。また赤色光源1の半値幅の短波長値が650nmを越えたり長波長値が750nm未満であると、上記したターン数の進行に伴う吸光曲線の形状変化の影響が大きくなり、従来と同様の問題を残すこととなる。なお、赤色光源1の中心波長値は690～700nmとすることが好ましく、実際にはこのような発光スペクトルを持つ赤色LEDを用いれば、長期間にわたり安定した測定が可能である。

【図1】



【0012】

【実施例】ニッケル濃度を5.58g/Lの一定値に保った無電解ニッケルめっき液について、中心波長710nm、半値幅±10nmの赤色光源を用いた従来法と、中心波長695nm、半値幅±90nmの赤色光源を用いた本発明法とによって、ニッケル濃度を測定した。ターン数が0のときには従来法による測定値も本発明法による測定値も、化学分析値5.6g/Lと一致していた。しかし、ターン数が5となると従来法によるニッケル濃度の測定値は6.5g/Lとなり、誤差は16%となった。これに対して本発明法によるニッケル濃度の測定値は5.7g/Lとなり、誤差は僅か2%にまで減少した。

【0013】

【発明の効果】以上に説明したように、本発明のニッケル濃度測定方法によれば、吸光度法のための赤色光源として広い波長領域にわたる連続スペクトル光源を用いたことにより、ターン数の進行に伴う吸光曲線の形状変化の影響を無くし、ターン数が進んでも吸光光度法により正確にニッケル濃度を測定することができる利点がある。また本発明は赤色光源を変えるだけで、容易に従来の測定装置に適用できる利点もある。よって本発明は無電解ニッケルめっき液のニッケル濃度管理を行ううえで効果の大きいものである。

【図面の簡単な説明】

【図1】吸光光度法の測定原理図である。

【図2】ニッケル濃度と吸光度との関係を示すグラフである。

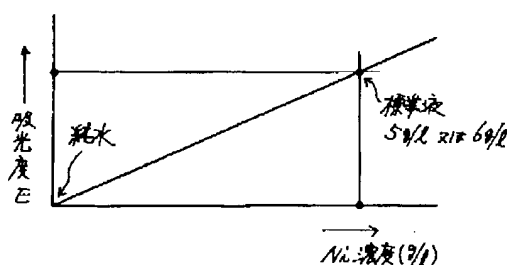
【図3】ターン数と吸光度から求めたニッケル濃度との関係を示すグラフである。

【図4】ターン数と吸光曲線との関係を示すグラフである。

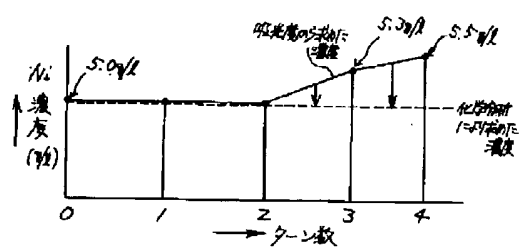
【符号の説明】

- 1 赤色光源
- 2 サンプリングされた無電解ニッケルめっき液
- 3 受光器

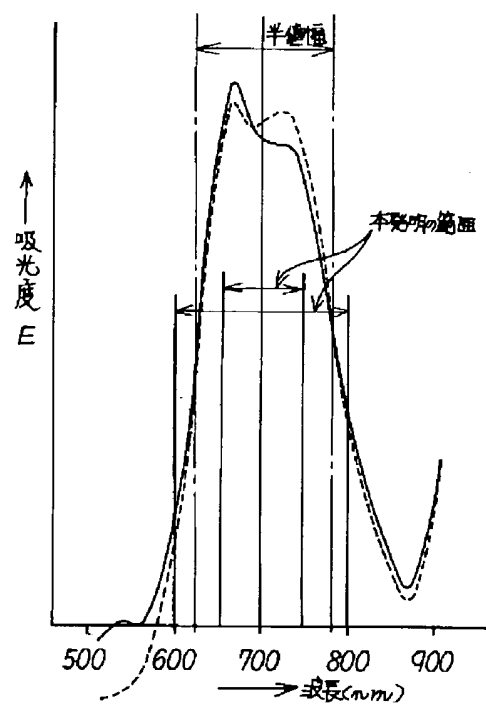
【図2】



【図3】



【図4】



PATENT ABSTRACTS OF JAPAN

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(21)Application number : **08-298432** (71)Applicant : **CHUO SEISAKUSHO LTD**

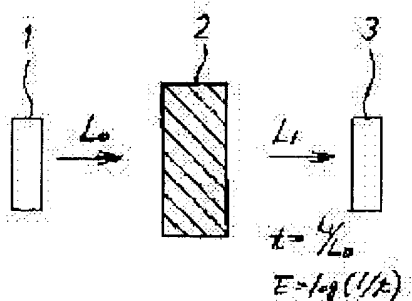
(22)Date of filing : **11.11.1996** (72)Inventor : **TSUGE YOSHIO**
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TAKEUCHI JIRO

(54) NICKEL CONCENTRATION MEASURING METHOD OF NONELECTROLYTIC NICKEL PLATING SOLUTION

(57)Abstract:

PROBLEM TO BE SOLVED: To enable accurate measurement in absorptiometry even if the number of turns proceeds by using a continuous spectrum light source having a specific short wavelength of half width and a specific long wavelength as a red light source.

SOLUTION: A continuous spectrum light source with a short wavelength of half width of 600 to 650nm and a long wavelength of 750 to 800nm is used as a red light source 1. Letting the amount of incident light irradiating a nonelectrolytic nickel plating solution 2 from the red light source 1 be L_0 and the amount of transmission light entering a light receiver 3 be L_1 , it is possible to obtain the nickel concentration of an electrolytic plating solution 2 from the equation; absorbance $E = \log(1/t)$ (transmittance: $t = L_1/L_0$). By this, it is possible to measure with accuracy by eliminating the



effects of change in shape of an absorbance curve associated with the process of turn number.

CLAIMS

[Claim(s)] [Claim 1] the nickel concentration of non-electrolyzed nickel-plating liquid -- the red light source -- using -- an absorptiometry -- measuring -- hitting -- as this red light source -- the short wavelength value of half-value width -- 600-650nm and a long wave -- a long value -- 750-800nm it is -- the nickel density measurement approach of the non-electrolyzed nickel-plating liquid characterized by using the continuous source.

[Claim 2] a main wave number -- 690-700nm it is -- the nickel density measurement approach of non-electrolyzed nickel-plating liquid according to claim 1 of using the red light source

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Field of the Invention] This invention relates to the nickel density measurement approach of the non-electrolyzed nickel-plating liquid by the absorptiometry.

[0002] [Description of the Prior Art] The nickel ion in plating liquid deposits as a nickel metal on a work-piece front face by the catalytic reduction reaction of a work-piece metal, and along with it, nickel concentration, reducing-agent concentration, pH, etc. fall gradually, and go by non-electrolyzed nickel plating. Therefore, plating liquid is sampled, nickel concentration is measured with an absorptiometry, and plating liquid management maintained at the value which was always able to define the amount of nickel in plating liquid etc. is performed.

[0003] Nickel density measurement by this absorptiometry is performed using the red light source with the wavelength near the absorption wavelength of nickel ion, and the red light source which was extracted to the narrow range of 710**10nm in the wavelength field with the filter in many cases is used. However, although the nickel concentration measured by this approach was in agreement with actual nickel concentration (chemical analysis) at the time of an initial make-up of electrolytic bath, when the number of turns (whenever [use]) progressed, there was a problem that an error became large. The cause is for change of a color tone to arise, when impurities, such as phosphorous acid and sodium sulfate, are accumulated if plating liquid ages and goes, and for change of a color tone to arise also by change of pH accompanying advance of the number of turns. An example of change of the absorbance by the change of the number of turns and pH in the case of 710**10nm of wavelength fields is shown in Table 1 and Table 2 for reference.

[0004] [0005]

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned conventional trouble, and it is made in order to offer the nickel density measurement approach of the non-electrolyzed nickel-plating liquid which can measure nickel concentration correctly with an absorptiometry, although the number of turns progresses.

[0006] [Means for Solving the Problem] this invention made in order to solve the above-mentioned technical problem -- the nickel concentration of non-electrolyzed nickel-plating liquid -- the red light source -- using -- an absorptiometry -- measuring -- hitting -- as this red light source -- the short wavelength value of half-value width -- 600-650nm and a long wave -- a long value -- 750-800nm it is -- it is characterized by using the continuous source. in addition, the main wave number -- 690-700nm it is -- things are desirable. Thus, this invention is 100-200nm about half-value width to having used the

red light source extracted to the narrow range whose conventional absorptiometry is the main wavelength of $710\pm 10\text{nm}$. The point is in the point using the continuous source made into the large width of face to say.

[0007] [Embodiment of the Invention] The gestalt of desirable operation of this invention is shown below. Drawing 1 is the measurement principle Fig. of an absorptiometry, and the non-electrolyzed nickel-plating liquid with which the red light source and 2 were sampled for 1, and 3 are electric eyes. When the amount of incident light irradiated by non-electrolyzed nickel-plating liquid 2 from the red light source 1 is set to L_0 and the amount of transmitted lights included in an electric eye 3 is set to L_1 , it is $t=L_1 / L_0$. It is called permeability and $E=\log (1/t)$ is called absorbance. And since nickel concentration is generally in direct proportion to an absorbance E as shown in drawing 2, it can ask for the nickel concentration in non-electrolyzed nickel-plating liquid from an absorbance E .

[0008] However, although the nickel concentration called for by the chemical analysis is fixed as shown in drawing 3 since impurity ion will be accumulated or pH will change if the number of turns progresses as described above, the concentration for which it asked from the absorbance increases, and a measurement error is produced. As a result of considering change of this absorbance, this invention person etc. solved changing like drawing 4, when the number of turns progressed, although nickel concentration had the fixed configuration of the extinction curve of non-electrolyzed nickel-plating liquid.

[0009] Namely, although an extinction curve is the configuration of the continuous line of drawing 4 at the time at the time of an initial make-up of electrolytic bath (zero turn), it changes to the configuration of the chain line of drawing 4 at the time of 5.07 turns. Therefore, by the approach using the red light source of the $710\pm 10\text{nm}$ conventional wavelength field, although nickel concentration is fixed, if the number of turns progresses, a result from which an absorbance E changes will be brought.

[0010] on the other hand -- this invention -- as the red light source 1 -- the short wavelength value of half-value width -- 600-650nm and a long wave -- a long value -- 750-800nm it is -- the continuous source is used. This wavelength field is mostly equivalent to the half-value width of an extinction curve shown in drawing 4 with a broken line. As shown in drawing 4, the configuration of an extinction curve has the part which will increase if the number of turns progresses, and the part which decreases. Since the amount L_1 of transmitted lights included in an electric eye 3 is the integral value of the section from the minimum wavelength value of the red light source 1 to the longest wave number, if an absorbance is measured using the continuous source covering a large wavelength field like this invention, the part which will increase if the number of turns progresses, and the part which decreases negate it mutually, and it can obtain an almost fixed absorbance.

[0011] If the short wavelength value of the half-value width of the red light source 1 becomes under 600 nm or a long wave number exceeds 800 nm, the sensibility to nickel concentration will fall. Moreover, the short wavelength value of the half-value width of the red light source 1 will exceed 650 nm, or the effect of the formation of a form status change of the extinction curve accompanying advance of the number of turns described above as a long wave number is under 750 nm will become large, and the same problem as usual will be left. In addition, the main wave number of the red light source 1 is 690-700nm. It is the red LED in which carrying out is desirable and it has such an emission spectrum in fact. If it uses, the measurement stabilized over the long period of time is

possible.

[0012] [Example] They are 5.58g/L about nickel concentration. About the non-electrolyzed nickel-plating liquid maintained at constant value, nickel concentration was measured by the conventional method which used the with the main wavelength of 710nm, and a half-value width [of $\approx 10\text{nm}$] red light source, and this invention method using the with the main wavelength of 695nm, and a half-value width [of $\approx 90\text{nm}$] red light source. When the number of turns was 0, the measured value by the conventional method and the measured value by this invention method were in agreement with chemical-analysis 5.6 g/L. However, when the number of turns was set to 5, the measured value of the nickel concentration by the conventional method became 6.5 g/L, and the error became 16%. On the other hand, the measured value of the nickel concentration by this invention method became 5.7 g/L, and errors were few or decreased even to 2%.

[0013] [Effect of the Invention] As explained above, although the effect of the formation of a form status change of the extinction curve accompanying advance of the number of turns is lost and the number of turns progresses, according to the nickel density measurement approach of this invention, there is an advantage which can measure nickel concentration correctly with an absorptiometry by having used the continuous source covering a wavelength field large as the red light source for an absorptiometry.

Moreover, this invention only changes the red light source, and also has an advantage easily applicable to the conventional measuring device. Therefore, when performing nickel concentration management of non-electrolyzed nickel-plating liquid, effectiveness of this invention is large.

PRIOR ART

[Description of the Prior Art] The nickel ion in plating liquid deposits as a nickel metal on a work-piece front face by the catalytic reduction reaction of a work-piece metal, and along with it, nickel concentration, reducing-agent concentration, pH, etc. fall gradually, and go by non-electrolyzed nickel plating. Therefore, plating liquid is sampled, nickel concentration is measured with an absorptiometry, and plating liquid management maintained at the value which was always able to define the amount of nickel in plating liquid etc. is performed.

[0003] Nickel density measurement by this absorptiometry is performed using the red light source with the wavelength near the absorption wavelength of nickel ion, and the red light source which was extracted to the narrow range of $710\approx 10\text{nm}$ in the wavelength field with the filter in many cases is used. However, although the nickel concentration measured by this approach was in agreement with actual nickel concentration (chemical analysis) at the time of an initial make-up of electrolytic bath, when the number of turns (whenever [use]) progressed, there was a problem that an error became large. The cause is for change of a color tone to arise, when impurities, such as phosphorous acid and sodium sulfate, are accumulated if plating liquid ages and goes, and for change of a color tone to arise also by change of pH accompanying advance of the number of turns. An example of change of the absorbance by the change of the number of turns and pH in the case of $710\approx 10\text{nm}$ of wavelength fields is shown in Table 1 and Table 2 for reference.

[0004]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the measurement principle Fig. of an absorptiometry.

[Drawing 2] It is the graph which shows the relation between nickel concentration and an absorbance.

[Drawing 3] It is the graph which shows the relation between the number of turns, and the nickel concentration for which it asked from the absorbance.

[Drawing 4] It is the graph which shows the relation between the number of turns, and an extinction curve.

[Description of Notations]

1 Red Light Source

2 Sampled Non-Electrolyzed Nickel-Plating Liquid

3 Electric Eye

DRAWINGS
